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The Effects of Acids and Alkalies on the Viscous and Structural Properties of Protoplasm

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Protoplasm becomes highly elastic, glutinous and fibrous, exhibits syneresis and changes from yellow to orange at the anode of an electric circuit. At the cathode, all properties are the opposite of those at the anode; the protoplasm becomes soft, lacks elastic, glutinous and fibrous qualities, shows no syneresis and becomes green in color. The change from the normal, which is intermediate, is due to the acid condition set up at the anode and the alkaline condition set up at the cathode. The anomalous (non-Newtonian) behavior of protoplasm, as well as its other characteristic jelly properties (imbibition, syneresis, coagulation, thixotropy, etc.) are attributed to the structural continuity which is responsible for the elastic qualities.

THE protoplasm of slime-moulds reacts in one of two definite and characteristic ways when traversed by an electric current. At the cathode the protoplasm becomes a fibrous mass, highly elastic (extensile), glutinous (adhering tenaciously to the dissection needle), resists the passage of a needle through it as would an entanglement of threads, gives every indication of possessing structural continuity, and undergoes syneresis. At the anode, the reverse situation arises in every particular. The protoplasm there becomes plastic (in the sense of lacking elasticity), resembles soft butter, is devoid of rigidity and extensibility, shows no tendency to adhere to a dissection needle, offers little resistance to the passage of a needle and exhibits no syneresis. Normal protoplasm is intermediate between these two conditions, i.e., it possesses all of the properties above enumerated as effects of the cathode, but to a less degree.

The material in the present experiments was the living protoplasm of *Physarum polycephalum;* the current came from a 4-volt dry cell; the electrodes were fine platinum needles.

A further striking change which takes place at both cathode and anode gives a clue to the cause of the other changes. This particular slime-mould, *Physarum*, contains a yellow pigment (possibly a lyochrome) which is an excellent *pH* indicator, with a color range from brilliant green through yellow to deep red orange, corresponding to a *pH* range of from 8 to 1.5.[1] At the cathode, the normally yellow protoplasm ($pH=6.2$) becomes bright green ($pH=8$); at the anode, it becomes a rich gold ($pH=3.5$ to 1.5).

When electrodes project into an electrolytic solution, an alkaline condition arises at the cathode and an acid condition arises at the anode. It is obvious then that alkalinity and acidity may be the factors involved in causing the above enumerated changes in protoplasm.

Most, though not all, of the changes produced by the current (i.e., the acid and alkaline conditions established by the current) are duplicated through the addition of acids and alkalies to the protoplasm. In the main, the "current" effects are reproduced by HCl, NaOH and NH_4OH; thus, when either of these two alkalies is added, the protoplasm becomes green in color, fibrous ("stringy"), tenacious, and highly elastic; and when HCl is added the protoplasm becomes orange in color, butter-like, and poorly extensile. (Other acids, acetic, phosphoric, etc., do not duplicate the situation so well.)

[1] W. Seifriz and M. Zetzmann, Protoplasma **22** (in press) (1935).

Protoplasm is an extremely heterogeneous system so that it is impossible to state which of its constituents is primarily responsible for the changes here recorded. It can only be said that a lyophilic material exists within it which reacts in two diametrically opposite ways to acids and alkalies.

The nearest approach to an analogy in the non-living world is the gelation and solation of colloidal systems by an electric current. Freundlich and Rawitzer[2] found that an electric current solidifies the thixotropic iron-oxide sol, while Karrer[3] found it to liquefy a thixotropic clay paste. That acid and alkali are responsible here also, and not the current as such, seems likely, as the iron-oxide is positive and would be affected by the negative OH^- ion, while the clay is negative and would respond to the positive H^+ ion.

The best analogy which helps toward an interpretation of the existence of such diverse qualities in the same substance when under different influences, is that of two soaps.[4] Two samples, from different manufacturers, of presumably the same kind of soap (sodium stearate) proved to be quite different in their physical properties. One, when of low concentration and low viscosity, supported within itself a small metal particle, and proved to be highly elastic; the other, at a much greater concentration and viscosity, would not support the particle and was wholly inelastic. Microscopic examination of the elastic soap revealed long, slender crystals within the thin solution, while similar examination of the inelastic soap showed it to be composed of irregularly shaped granules. The elastic soap possessed a certain degree of rigidity due to a fibrous structure, while the inelastic soap lacked this quality because it was granular. The case of protoplasm is similar; the highly extensile protoplasm at the cathode exhibits rigidity and has a fibrous structure, while the butter-like protoplasm at the anode gives no indication of such a quality or structure. In short, elasticity in organic colloidal systems rests upon a fibrous framework of linear and crystalline units. Upon this structure do typical jelly qualities depend—elasticity, rigidity (particularly evident in firm gels where the solid content is low, 0.2 percent, in proportion to the amount of water), imbibition (the taking in of water *with swelling*), thixotropy, syneresis and anomalous (non-Newtonian) behavior.

There have been attempts to regard the fundamental structure of protoplasm as that of an emulsion, just as was formerly done for non-living colloidal jellies, a misconception which gave rise to the misnomer "emulsoid." Protoplasm has also been regarded as a true solution because no yield value was discovered. Both are impossible conceptions of a system which exhibits all of the properties of jellies (the dry weight of protoplasm is 55 percent protein).

It has been maintained that the structural framework responsible for the elasticity of lyophilic solutions, such as thin solutions of proteins, soaps, etc., is not necessarily responsible for their deviation from Poiseuille's law of true viscous flow, because other non-Newtonian systems are not elastic. Theoretically, viscosity and elasticity are independent variables, but they do not appear to be so experimentally, in that no colloidal system is known which is elastic and yet exhibits true viscous flow. In a mathematical discussion of this problem, Weissenberg[5] indicates the complexity of the situation. He defines three types of pure systems and develops therefrom three theories based on the three pure properties of relaxation, elasticity, and friction. He points out that only when these properties are pure (i.e., alone and functioning separately) can the linear relationships (the single constant laws of Maxwell, Newton, and Hooke) hold. The laws of viscosity and elasticity were developed for homogeneous bodies only, and, therefore, hold in such systems only, e.g., viscosity in glycerine and elasticity in steel. When they are combined, the situation becomes exceedingly complex, and is impossible of precise mathematical interpretation.

The claim that there is no reason to believe certain non-Newtonian hydrocarbon oils to be elastic, would have to be verified. The work on

[2] H. Freundlich and W. Rawitzer, Kolloid Zeits. **41**, 102 (1927).
[3] E. J. Karrer, J. Rheology **3**, 334 (1932).
[4] W. Seifriz, Colloid Sym. Monog. **3**, 285 (1925).
[5] K. Weissenberg, Mitt. d. deut. Materialprüfungsanstalten **19**, 54 (1932).

synthetic rubber by Carothers[6] and others, shows certain hydrocarbon oils to be elastic. The natural rubber hydrocabron can be purified by methods of extraction to such a point that it has only an exceedingly minute nitrogen content. This purified product retains practically all of the properties of rubber. Some synthetic rubbers may be obtained in the form of pure hydrocarbons; for example, isoprene can be polymerized merely by heating it or exposing it to very high pressure. The product is definitely rubber-like, i.e., highly elastic, and essentially pure hydrocarbon. The commerical synthetic rubber, duprene, is made from a chlorine containing compound, chloroprene, which is structurally analogous to isoprene. This pure synthetic rubber has the composition C_4H_5Cl, and hence is not a hydrocarbon, but it can be obtained in a form which shows a typically rubber-like behavior without the addition of any protein to it, or any other materials that might in themselves confer an elastic structure.

All recent work on colloidal jellies indicates that they are built up of long, tenuous, crystalline fibers which interlock to form an elastic framework, or, as in the case of cellulose, the linear units (molecules, micelles, or crystallites) may be arranged in an orderly fashion, as in ramie, or at random as in cellophane.[7–9]

It is of further interest and of fundamental significance that sinew, keratin, hair, silk, muscle, nerve, and brain (the last three are protoplasm) give spectrograms (x-ray diffraction patterns), thus indicating a crystalline character.

In this connection polarization studies reveal some facts of interest. While they have not shown protoplasm in general to be anisotropic, they have shown that striped muscle and all other contractile tissue is anisotropic. Scarth[10] has demonstrated that chlorophyll, a common constituent of some plant cells, is anisotropic.

Protoplasm is a system closely comparable to gelatin, albumin, and similar lyophilic systems. It possesses all the properties of organic jellies (elasticity, thixotropy, etc.). These properties exist in virtue of a continuity in structure. They are greatly accentuated in protoplasm by the addition of alkalies, and reduced (often wholly eliminated) by the addition of certain acids, whether these are added separately or produced at the cathode and anode of an electric circuit.

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[6] W. H. Carothers *et al.*, J. Am. Chem. Soc. **53**, 4203 (1931).

[7] W. H. Carothers, Chem. Rev. **8**, 353 (1931).

[8] K. H. Meyer and H. Mark, *Der Aufbau der Hochpolymeren Organischen Naturstoffe*, Leipzig (1930).

[9] W. Seifriz, Protoplasma **21**, 129 (1934).

[10] G. W. Scarth, Quart. J. Exp. Physiol. **14**, 99 (1924).

A New Feature in the Calibration of a Capillary-Tube Viscometer

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Because of deviations from a truly cylindrical surface at the capillary wall or to an abnormal orifice at one end of the capillary, the value of the coefficient, m, of the kinetic energy correction may be abnormally high with one direction of flow while it remains quite normal with the other direction. This variation may even cause the value of the principal instrumental constant, C, to be slightly greater in one direction of flow than in the opposite. This effect has been shown to be definitely greater than experimental error and is thought to be due to a slight difference in the "effective" capillary radius in the two directions of flow. This study shows the necessity of determining both m and C for each direction of flow through the capillary. This suggests the use of two viscosity formulas: $\eta = C_l p_0 t - m_l C' \rho / t$ for "left-hand data," and $\eta = C_r p_0 t - m_r C' \rho / t$ for "right-hand data." Although a well-constructed viscometer may not require this unusual precaution, with it any commercially made capillary viscometer may be used with the highest possible accuracy.

THIS study resulted directly from anomalies which became apparent in calibrating a viscometer of the Bingham-Jackson[1] design with the ends of the capillary cut off squarely without flanging. If the two reservoirs of a viscometer are not at the same level or if they differ in shape or size, a resultant hydrostatic head will cause a more rapid rate of flow in one direction than in the reverse direction. The difference in the times of flow in the two directions due to this hydrostatic head usually becomes greater as the times of flow become longer. In the preliminary work with viscometer, Nos. 1–32, the authors noticed that while a rather large difference in times of flow in the two directions was observed when the total time was short, when the time of flow became long, the difference in times of flow in the two directions became quite small. The apparent hydrostatic head plotted against average time of flow is shown in Fig. 1.

It became obvious that the absurdly large values of the hydrostatic head calculated from determinations at less than 1000 seconds flow time were due to an improperly applied correction for kinetic energy. Since the general equation for the hydrostatic head involves an approximate value for the constant, C, and an uncertain value for m, the coefficient for the kinetic energy correction, the authors decided to avoid these uncertainties by determining the hydrostatic head under conditions where the kinetic energy correction became negligible, using the specific equation, $h = p_0(t_l - t_r)/2\rho t$, where p_0 and t are average values of pressure and time of flow. A similar procedure has been recommended by Bingham and Geddes.[2] With determinations where the times of flow were from 1000 to 2000 seconds, a hydrostatic head of 0.02 cm was calculated, the right reservoir being effectively that much higher than the left. This value was used exclusively throughout the research.

The instrument was then further calibrated at 20°C with freshly distilled, dust-free water having a specific conductance of 1.59×10^{-6} mho per cm, assuming it to possess a viscosity of 1.0050 centipoises. Eight pressures from 100 to 380 g/cm² were employed. A summary of the data taken with the external pressure applied to the left limb of the viscometer is given in Table I,

TABLE I. *A summary of calibration data for viscometer, Nos. 1–32, pressure applied only to the left limb (20°C).*

TIME (sec.)	PRESSURE p_0	C (m = 0.00)	C (m = 1.12)	m (C = 1.4718)	C (m = 3.05)	m (C = 1.4736)	C (m = 3.31)
674.5	101.90	1.4622	1.4661	2.801	1.4723	3.326	1.4736
674.6	101.90	1.4620	1.4658	2.860	1.4724	3.385	1.4733
494.0	139.50	1.4584	1.4636	2.871	1.4726	3.256	1.4738
493.9	139.50	1.4587	1.4639	2.805	1.4729	3.191	1.4741
385.0	179.56	1.4538	1.4605	3.015	1.4720	3.316	1.4735
385.0	179.55	1.4539	1.4605	2.981	1.4721	3.300	1.4736
316.5	219.08	1.4494	1.4575	3.094	1.4715	3.342	1.4734
316.5	219.05	1.4496	1.4577	3.066	1.4717	3.314	1.4736
266.7	260.66	1.4456	1.4553	3.045	1.4718	3.255	1.4740
266.7	260.66	1.4457	1.4553	3.045	1.4718	3.255	1.4740
233.4	298.72	1.4415	1.4524	3 103	1 4712	3.287	1.4738
234.3	297.61	1.4413	1.4522	3.136	1.4709	3.321	1.4735
207.9	336.31	1.4374	1.4496	3.238	1.4707	3.312	1.4736
208.0	336.27	1.4369	1.4491	3.287	1.4702	3.360	1.4730
186.1	376.98	1.4325	1.4462	3.229	1.4696	3.377	1.4728
186.1	376.95	1.4326	1.4463	3.221	1.4696	3.368	1.4729
	Average		1.4564	3.050	1.4715	3.310	1.4736
	Average error		±0.0056	±0.122	±0.0008	±0.039	±0.0003
			0.39%	4.0%	0.05%	1.2%	0.02%

[1] Bingham and Jackson, U. S. Bur. Stand. Bull. No. 298, **14**, 59 (1917).

[2] Bingham and Geddes, Physics **4**, 203 (1933).

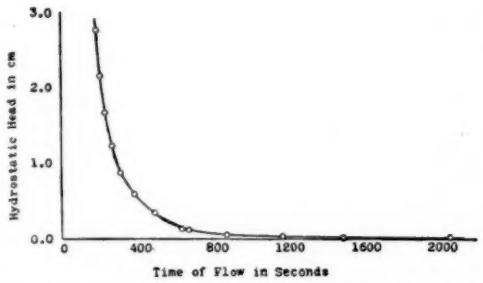

FIG. 1. "Apparent" hydrostatic head resultant in the viscometer versus time of flow.

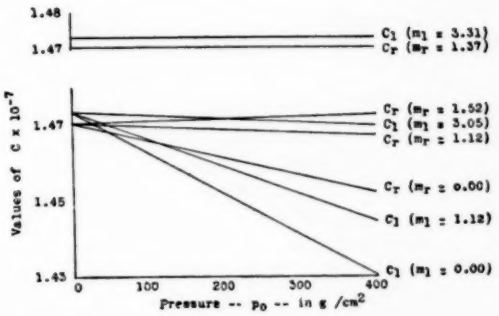

FIG. 2. Values of C as a function of pressure.

and the corresponding data with the pressure applied to the right limb are given in Table II. The data have been called "left-hand data" and "right-hand data," respectively.

The constant, C, was first determined by using $m_l = m_r = 1.12$ as has been customarily assumed for capillaries with ends cut off squarely.[3] The results are given in the fourth column of Tables I and II, and are plotted against pressure in Fig. 2. The slopes of these curves indicate that m_r and especially m_l were incorrectly assumed. Bingham and Geddes[2] have indicated the desirability of determining m for both directions of flow, and a method of calculating m has been furnished by Bingham and Thompson.[4] $m = (C - C_0)p_0 l^2/C'\rho$, where $C' = V/8\pi l$. The values of $C_0(m = 0.00)$ are given in the third column of Tables I and II and are also plotted in Fig. 2. The equations of these curves were determined by the method of averages, and the "true" value of C determined as the intercept where p_0 is zero. The value, 1.4718×10^{-7}, was found to be the average of four intercepts.

TABLE II. *Condensed calibration data for viscometer, Nos. 1–32, pressure applied only to the right limb (20°C).*

TIME (sec.)	PRESSURE p_0	C (m = 0.00)	C (m = 1.12)	m (C = 1.4718)	C (m = 1.52)	m (C = 1.4708)	C (m = 1.37)
673.0	101.95	1.4648	1.4687	2.034	1.4701	1.744	1.4695
491.6	139.54	1.4651	1.4703	1.422	1.4722	1.210	1.4715
382.5	179.59	1.4632	1.4700	1.422	1.4724	1.257	1.4715
314.0	219.09	1.4609	1.4692	1.489	1.4721	1.353	1.4709
264.2	260.71	1.4591	1.4689	1.461	1.4724	1.346	1.4710
231.3	298.17	1.4576	1.4687	1.430	1.4727	1.330	1.4712
205.3	336.32	1.4556	1.4682	1.450	1.4726	1.361	1.4709
183.4	376.99	1.4536	1.4676	1.452	1.4726	1.373	1.4707
	Average		1.4689	1.520	1.4721	1.372	1.4708
	Average error		±0.0007	±0.127	±0.0005	±0.093	±0.0004
			0.05%	8.4%	0.04%	6.8%	0.03%

[3] Bingham, *Fluidity and Plasticity*, p. 18.
[4] Bingham and Thompson, J. Rheology **1**, 418 (1930).

Assuming $C = 1.4718 \times 10^{-7}$, m_l and m_r were calculated and the results are given in the fifth column of Tables I and II, respectively. The value of m_l, 3.05, is abnormally high probably due to an unevenness or constriction (invisible to the eye) at the lower and exit end of the capillary for this direction of flow. In the sixth column of Tables I and II are given values of C calculated using $m_l = 3.05$ and $m_r = 1.52$. The values deviate from the mean by an average of 0.05 percent.

It will be observed from Fig. 2 that the several curves do not give a common intercept (when p_0 is zero) as was expected. Neither do the intercepts come at several variant points due to experimental errors. There are two distinct intercepts. The values of C from "right-hand data" approach 1.4708×10^{-7} while values of C from "left-hand data" approach 1.4736×10^{-7}. The idea of having a different value of C for each direction of flow is both new and perplexing because C represents $\pi g R^4/8Vl$ where each value is supposedly a constant. The fact is undeniable, however, for the difference between the two constants is considerably greater than the experimental error. Evidently because of the irregularities in the surface and other possible deviations from a truly cylindrical surface, the "effective or viscometric radius" of the capillary differs slightly in the two directions of flow.[5]

By investigating the desirability of recognizing two values for C, namely, $C_l = 1.4736 \times 10^{-7}$ and $C_r = 1.4708 \times 10^{-7}$, new values of m_l and m_r were calculated and are given in the seventh column of Tables I and II. Finally in the eighth column are

[5] This effect may be attributed to a Couette correction which is different for each direction of flow. Possibly, a more accurate statement would be that there exist *in effect* two values of R^4/l, one for each direction of flow.

TABLE III. *Average accuracy attained.*

	(A)	(B)	(C)
m_l	1.12	3.05	3.31
m_r	1.12	1.52	1.37
C_l	1.4718	1.4718	1.4736
C_r	1.4718	1.4718	1.4708
16 lefts	1.07%	0.05%	0.02%
16 rights	0.20%	0.06%	0.04%
16 pairs	0.64%	0.03%	0.03%

given values of C calculated with the new values, $m_l=3.31$ and $m_r=1.37$. These values deviate from their means by an average of from 0.02 to 0.03 percent. By the method of averages the data in Tables I and II have been equated as follows:

where $(m=0.00)$ $C_l=1.47303-0.00010640\ \dot{p}_0$
$(m=1.12)$ $C_l=1.47323-0.00007056\ p_0$
$(m=3.05)$ $C_l=1.47364-0.00000910\ p_0$
$(m=3.31)$ $C_l=1.47378-0.00000103\ p_0$
Reported $C_l=1.4736\times10^{-7}$

$(m=0.00)$ $C_r=1.47062-0.00004462\ p_0$
$(m=1.12)$ $C_r=1.47076-0.00000767\ p_0$
$(m=1.52)$ $C_r=1.47078+0.00000562\ p_0$
$(m=1.37)$ $C_r=1.47076+0.00000063\ p_0$
Reported $C_r=1.4708\times10^{-7}$.

All eight of these curves are shown in Fig. 2.

The resultant accuracy of our viscometric determinations was estimated by calculating the viscosity of water from the calibration data in Tables I and II using (*A*) $m_l=m_r=1.12$ and $C=1.4718\times10^{-7}$, (*B*) $m_l=3.05$, $m_r=1.52$ and $C=1.4718\times10^{-7}$ and (*C*) $m_l=3.31$, $m_r=1.37$, $C_l=1.4736\times10^{-7}$ and $C_r=1.4708\times10^{-7}$. The deviations of the results from the assumed 1.0050 centipoises were noted. The individual errors of sixteen "left limb" determinations were averaged; the individual errors of sixteen "right limb" determinations were averaged; and finally the errors of the sixteen left-right averaged pairs were averaged. The results are summarized in Table III. The results under (*B*) and (*C*) are much better than those under (*A*), and when individual determinations using but one direction of flow are to be relied upon, the constants under (*C*) produce the best results.

TABLE IV. *Comparison of fluidities of ethyl cyanide using (B) $m_l=3.05$, $m_r=1.52$ and $C_l=C_r=1.4718\times10^{-7}$ and (C) $m_l=3.31$, $m_r=1.37$, $C_l=1.4736\times10^{-7}$ and $C_r=1.4708\times10^{-7}$.*

Temp. °C	Limb	(B) Fluidity	(B) Ave. Fluidity	(C) Fluidity	(C) Ave. Fluidity
0.00	L	183.76		183.72	
"	R	183.64	183.70	183.68	183.70
10.00	L	206.83		206.80	
"	R	206.54	206.69	206.54	206.67
20.00	L	230.72		230.77	
"	R	230.89	230.81	230.85	230.81
30.00	L	255.82		255.91	
"	R	256.03	255.93	255.94	255.93
40.00	L	281.75		282.00	
"	R	282.44	282.10	282.28	282.14
60.00	L	337.50		338.05	
"	R	338.60	338.05	338.24	338.15
80.00	L	398.26		399.30	
"	R	400.42	399.34	399.78	399.54
Minimum deviation		0.033%		0.006%	
Maximum deviation		0.271%		0.063%	
Average deviation		0.105%		0.034%	

Finally, the determination of fluidity of ethyl cyanide serves to illustrate the comparative accordance of the two calculations, (*B*) and (*C*). The comparison is shown in Table IV. At the bottom of the table are given the minimum, maximum and average deviations from the means for each method of calculation. It will be observed that while the averages under each system are almost identical, the complete calibration reduces the average error from 0.105 to 0.034 percent.

SUMMARY

1. Additional evidence has been offered to show the desirability of determining the hydrostatic head under conditions where the time of flow is so long that the kinetic energy correction will be negligible.

2. Even though an average of determinations in both directions of flow is to be made, it is unsafe to assume a fixed value for m.

3. A complete calibration is recommended for the greatest accuracy by determining C_l and C_r independently as mathematical intercepts and then calculating the corresponding values for m_l and m_r.

V. The Correlation of Distillation Range with the Viscosity of Creosote*

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(Received January 16, 1935)

The results of viscosity measurements of a series of creosotes distilled from a single tar are given. It was found that these creosotes are truly viscous solutions which permits the designation of the data as absolute viscosity. The viscosity-temperature data conform to two equations, one an empirical relationship previously found in an analogous series of crude oils, the other developed from theoretical considerations. It is remarkable that in spite of the complex nature of creosote, the viscosity data permit one to regard the material boiling below 355°C as solvent and the residue above that temperature as solute. This is not true for any other temperature limit customarily used in creosote analysis.

INTRODUCTION

ALTHOUGH all creosotes generally used in the wood preservation industry are distillates of coal tar, they may differ widely in the character and proportions of their constituents. Differences are mainly due to different methods of coal carbonization and subsequent distillation of the tars. At present the wood preservation industry is deeply concerned with the comparative utilities of high and low boiling creosotes which are dependent in part upon factors which are not readily stated in terms of differences in the character of the components. A direct comparison of high and low residue creosotes is usually complicated by the fact that the low residue creosotes are distilled from very different types of tar than are the high residue creosotes and may therefore differ radically from the latter in the character of the components.

Mr. W. H. Fulweiler of the United Gas Improvement Company, in connection with a special study for the American Wood-Preservers' Association, had kindly furnished us a series of creosotes distilled from a common tar but of various boiling ranges. We were thus offered the opportunity of studying eight creosotes differing presumably only in the relative amounts of their various constituents. The distillation analyses of these eight creosotes are given in Table I. The values given represent the percentages distilling in the indicated temperature range.

Experimental studies of these creosotes have been made concerning the correlation of distillation range with viscosity, surface tension, interfacial tension against water, and with capillary penetration into paper strips. Only the viscosity relationships are reported here.

A large amount of general information has been collected from observations of the practical problems involved in commercial impregnations and field tests which indicates that viscosity is an important factor in penetration, retention, permanence, and bleeding in creosote impregnated timber. This is to be expected on the basis of the work of Washburn[1] demonstrating penetration to be governed by the ratio of the surface tension to viscosity. The later work of Peek and McLean[2] and McLean and Kohman[3] has also demonstrated the importance of this ratio in the filling of irregular capillary pores. It seems opportune at this point to mention that unpublished experimental work on the surface tension and capillary penetration of these creosotes has not only verified the importance of the above-mentioned ratio but has also shown that the difference in rate of penetration of these creosotes into paper strips is due to their difference in viscosity since their surface tensions are constant for all practical purposes. Moreover, it is believed that a study of the viscosity of creosote may offer a means of identifying the various types of creosote in general use in the wood preservation industry. Since in commercial practice, the temperature of impregnation is relatively high whereas the temperature of subsequent exposure of treated timbers is comparatively low, it was decided to include a corresponding viscosity-temperature study.

* This paper is one of a series entitled "Chemical Studies of Wood Preservation" being published in this journal and in Industrial and Engineering Chemistry.

[1] Washburn, Phys. Rev. **17**, 273 (1921).
[2] Peek and McLean, Ind. and Eng. Chem. (Anal. Ed.) **6**, 85 (1934).
[3] McLean and Kohman, Elec. Eng. **53**, 255 (1934).

TABLE I. *Distillation analyses of Fulweiler creosotes.*

Temp. °C	F–1	F–2	F–3	F–4	F–5	F–6	F–7	F–8
0–170	—	—	—	—	—	—	—	—
170–205	0.99	0.75	0.98	0.21	1.47	1.48	1.85	2.29
205–210	1.08	0.77	1.18	1.33	0.90	1.51	1.40	2.09
210–235	8.10	8.32	11.63	11.84	14.25	18.09	22.21	27.99
235–245	5.11	5.81	7.11	6.83	8.11	8.61	9.99	10.26
245–270	11.93	12.66	12.71	14.32	15.34	16.11	16.07	15.96
270–300	8.92	9.65	10.60	10.55	11.68	10.80	11.45	11.32
300–315	4.19	4.24	4.56	5.47	4.77	5.86	5.69	5.32
315–355	15.69	17.36	19.97	20.73	22.15	21.59	18.93	16.00
Residue above 355°	43.84	40.25	31.11	28.52	20.85	15.49	12.21	8.49
Tar acids to 300° in cm³	4.47	4.50	5.30	5.25	5.80	6.65	7.25	8.13
Tar acids to 355° in cm³	8.3		8.5		9.6		12.0	
Benzene insoluble in %	0.06	0.08	0.08	0.14	0.09	0.07	0.08	0.06
Coke residue in %	0.61	0.59	0.47	0.67	0.76	0.51	0.68	0.41
Sulphonation residue 300–355° in %	0.9	0.9	1.1	0.9	0.7	0.7	0.7	0.8

POISEUILLE'S LAW

The passage of true fluids under external pressure through a uniform capillary tube of circular cross section for conditions of stream-line flow may be quantitatively expressed by Poiseuille's law,

$$\eta = \pi P r^4 t / 8 V l, \qquad (1)$$

in which η is the viscosity of the liquid, l is the capillary length, r the radius of the capillary and t is the time required for a volume (V) of the liquid to flow through the capillary tube under a pressure of P dynes per square centimeter.

When the rate of flow through the capillary tube is rapid the equation must be modified to correct for the kinetic energy and becomes:

$$\eta = \pi P r^4 t / 8 V l - V \rho / 8 \pi l t, \qquad (2)$$

where ρ is the density of the liquid.

It is seen that for any capillary tube viscometer in which a fixed volume (V) is forced through a capillary, the viscosity is related to the experimentally measured quantities, P and t, by

$$\eta = CPt - C'\rho/t, \qquad (3)$$

in which C is the viscosity constant of the instrument and C' is the constant for the kinetic energy correction.

EXPERIMENTAL

The apparatus used for the determination of the viscosity is of the type described by Bingham.[4] It consists essentially of a modified Ostwald viscometer having pressure-cocks so arranged that checks can be obtained by running the liquid back and forth from one bulb to the other. Each of the values given in the data represents the average of two such determinations.

A pressure tank was provided into which compressed nitrogen was admitted to build up the desired pressure. This tank was of sufficient size to prevent perceptible drop in the pressure during a determination.

The viscometer was submerged vertically in an oil bath which was maintained at the desired temperature with an accuracy of ± 0.1°C by means of a mercury column thermostatic control.

The constants of viscometer No. 2, which was used throughout this study, are as follows:

$r = 0.0278$ cm $\qquad C = 5.7448 \times 10^{-6}$
$V = 3.952$ cm³ $\qquad C' = 0.01780$
$l = 9.90$ cm.

In preparing for a set of determinations, the creosote was heated to 90°C to assure the solution of any crystals present at room temperature. The sample was thoroughly mixed and a suitable quantity pipetted into the viscometer. The filled instrument was placed in the oil bath which had previously been adjusted to the lowest desired temperature. After half an hour had elapsed the measurements were made according to Bingham.[4] The determinations were made at two or more pressures in order to determine

[4] Bingham, *Fluidity and Plasticity*, pp. 76 and 312.

whether the creosotes exhibited the flow characteristics of true solutions.

Viscosity observations of each creosote were made at successively higher temperatures to avoid the necessity of cleaning the small capillary of the viscometer after each determination. The determinations were made initially at the lowest temperature as the expansion of the creosotes with rise in temperature made it possible to adjust the working volume of the liquid without removing the instrument.

The viscosities of the Fulweiler creosotes as determined from the above measurements are recorded in Table III. Since it was found that the calculated viscosity values did not vary with pressure only the average value is given.

The densities used in the kinetic energy correction were determined at the various temperatures by means of water calibrated pycnometers and are tabulated in Table II.

TABLE II. *Absolute densities of Fulweiler creosotes.*

Sample No.	40°C	60°C	80°C	100°C
F–1	1.0892	1.0767	1.0610	1.0460
F–2	1.0843	1.0692	1.0555	1.0404
F–3	1.0716	1.0571	1.0429	1.0273
F–4	1.0695	1.0576	1.0416	1.0265
F–5	1.0639	1.0506	1.0346	1.0194
F–6	1.0550	1.0416	1.0254	1.0101
F–7	1.0507	1.0372	1.0208	1.0052
F–8	1.0418	1.0281	1.0120	0.9963

These densities of the Fulweiler creosotes also constitute added information on the physical properties. It can be seen that they decrease with content of high boiling material and with increase in temperature.

The fact that the viscosity values of the creosotes were independent of pressure when observed at constant temperature indicates that they are truly viscous solutions. Hence, since the viscosity is a constant relating shearing stress to velocity gradient, we may refer to the above-mentioned values as absolute viscosities and it is not necessary to specify the pressure of determination.

VISCOSITY-TEMPERATURE

It is a well-known fact that a creosote will grow less viscous as the temperature is increased, but the theoretical law for the change of viscosity with temperature is unknown and empirical methods must be employed in studying this relationship.

If the viscosity is plotted against the temperature there is obtained a series of more or less hyperbolic curves which are inconvenient for extrapolation purposes. It is therefore desirable to adopt a method of plotting or form of equation which will give approximate straight line relationships for creosotes.

TABLE III. *Change in viscosity of Fulweiler creosotes with temperature.*

Sample No.	% Residue above 355°C	Temp. °C	Viscosity poises
F–1	43.84	40	0.1064
		60	0.0544
		80	0.0320
		100	0.0218
F–2	40.25	40	0.0973
		50	0.0662
		60	0.0492
		80	0.0306
		100	0.0203
		120	0.0149
F–3	31.11	40	0.0675
		60	0.0377
		80	0.0243
		100	0.0170
F–4	28.52	40	0.0667
		60	0.0376
		80	0.0241
		100	0.0169
F–5	20.85	40	0.0525
		60	0.0310
		80	0.0211
		100	0.0148
F–6	15.49	40	0.0445
		60	0.0268
		80	0.0183
		100	0.0135
F–7	12.21	30	0.0531
		40	0.0396
		60	0.0247
		80	0.0170
		100	0.0125
F–8	8.49	40	0.0344
		60	0.0218
		80	0.0160
		100	0.0114
F–9*	0.00	40	0.0263
		60	0.0179
		80	0.0135
		100	0.0105

* F–9 is the designation for the material boiling below 355°C and the values listed were extrapolated from Fig. 4.

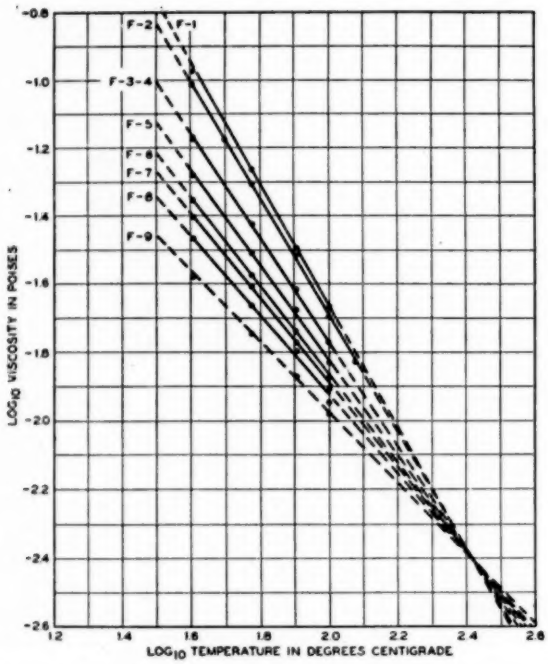

FIG. 1. Logarithmic viscosity-temperature diagram for Fulweiler creosotes.

Many equations have been suggested to fit the data relating the viscosity of various liquids to temperature. Some of these are based on theoretical considerations, but generally they have been developed merely as a means of correlating existing data. With the latter object in view, several of these equations were examined as to their possible application to the viscosity-temperature data of the Fulweiler creosotes. The two equations which were found to fit the data fairly accurately are the only ones discussed here.

Herschel[5] and others have made extensive studies of the viscosity of crude petroleum oils. They found that a logarithmic plot of viscosity *versus* temperature gave approximately straight lines over the temperature range studied. They also showed that if these lines were extended to higher temperatures they met approximately at a point, which was characteristic of the type of crude oil. Upon the application of this method to the creosotes in question, a series of converging straight lines was obtained as shown in Fig. 1. The general equation for these lines is expressed by the relationship of Oelschläger[6]

$$\log \eta = \log K - m \log t, \qquad (4)$$

in which K and m are constants, η is the viscosity and t is the temperature Centigrade. Bateman[7] used a similar equation for the relationship between viscosity and temperature of creosote and carbolineum oils.

The reason for the single point of intersection of the creosotes is not known at the present time but it is hoped that an extension of this work to other types of creosotes may establish the significance of this convergence. It is probable that the point of intersection is merely an indication that these creosotes are all members of the aromatic series of hydrocarbons but it may be due to the fact that they were distilled from the same tar. This opens up the interesting possibility that the location of this point of convergence may be an indication of the quality of the creosote.

A modified form of the Andrade[8] equation suggests a second viscosity-temperature relationship in the form:

$$\log \eta = a + b/(T - A), \qquad (5)$$

where a, b and A are constants of the liquid and T is the absolute temperature. A plot of $\log_{10} \eta$ against $1/(T-A)$, as shown in Figs. 2 and 2A, shows that this equation gives a very good straight line for these creosotes. It is not as adaptable as Eq. (4) as three constants are necessary for its determination. The values of A which were found necessary for the solution of the equation are given in Table IV.

TABLE IV. *Values of A necessary for the solution of Eq. (5).*

Sample No.	A	Sample No.	A
F–1	198	F–5	160
F–2	193	F–6	157
F–3	180	F–7	153
F–4	176	F–8	151
		F–9	148

The decrease of A with an increase of low boiling material is very noticeable as shown above but the scope of this paper does not permit the development of any specific conclusions from this fact. It is believed however that the constant

[5] Herschel, Ind. and Eng. Chem. **14**, 715 (1922).
[6] Oelschläger, Zeits. f. Ver. deut. Ing. **62**, 422 (1918).
[7] Bateman, U. S. Dept. Agr., Bull. 1036, 54.
[8] Andrade, Nature **125**, 581 (1930).

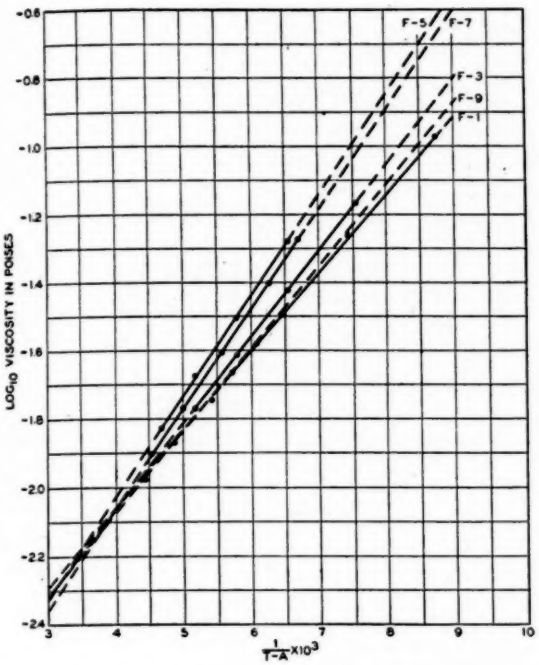

FIG. 2. Viscosity-temperature diagram for odd numbered Fulweiler creosotes.

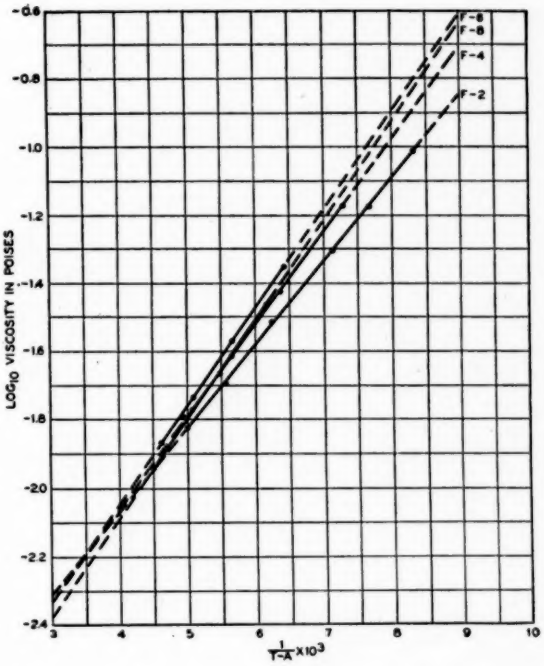

FIG. 2A. Viscosity-temperature diagram for even numbered Fulweiler creosotes.

A is in some manner connected with the boiling range or possibly the melting points of the creosotes.

VISCOSITY-RESIDUE BOILING ABOVE 355°C

It is generally believed that the viscosity of a creosote bears some relationship to the specific gravity when the gravities are compared at the same temperatures. Since this characteristic is largely determined by the concentration of high boiling material, it should be possible to establish some relationship between viscosity and distillation range in the creosotes studied.

Arrhenius[9] first proposed the equation:

$$\log \eta(\text{rel.}) = \theta C, \qquad (6)$$

in which θ is a constant depending on the temperature, C is the concentration of solute and η(rel.) is the viscosity of the solution divided by the viscosity of the solvent. Although this equation has been found to hold with considerable accuracy in the case of dilute solutions of non-electrolytes, it is not adaptable to the data listed above in its present form. However, if the equation is written in the form suggested by Berl[10] it becomes:

$$\log \eta = B + KC, \qquad (7)$$

where B and K are constants depending on the temperature of the solution and η is now the absolute viscosity.

In Fig. 3 the $\log_{10} \eta$ has been plotted against the concentration of material distilling above 355°C. The resulting curves show a remarkable rectilinearity over the distillation range of the creosotes studied which practically covers the boiling ranges of all commercial creosotes. These curves were extrapolated to zero concentration of material distilling above 355°C and the viscosities of the low boiling material so determined were designated as being those of a hypothetical creosote F–9. It is very interesting to note that when these values of viscosity were plotted against the temperature as shown in Figs. 1 and 2, the resulting curves followed the same general relationship as did the Fulweiler creosotes.

In order to determine whether Eq. (6) could be applied to these creosotes, assuming the extrapolated values of viscosity of F–9 (a hypo-

[9] Arrhenius, Zeits. f. physik. Chemie **1**, 285 (1887).

[10] Berl and Umstatter, Kolloid-Beihefte **34**, 1 (1931).

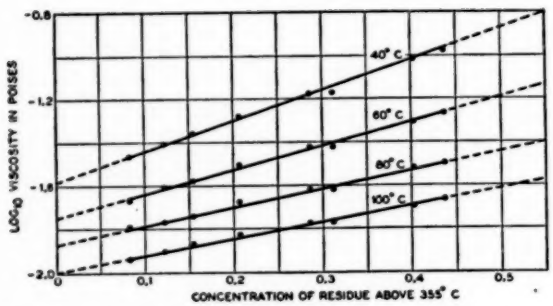

FIG. 3. Viscosity-concentration diagram for Fulweiler creosotes.

thetical creosote) to be those of a solvent, the ratio of $\log_{10} \eta$(rel.) divided by the concentration of material boiling above 355°C was determined. The constancy of this ratio, as shown in Table V, indicates that the above equation can be applied to these creosotes. This is unusual as it states that the materials boiling above and below 355°C in any of the eight creosotes may be considered as solute and solvent, respectively, with constant viscosities at any given temperature and that in these creosotes the viscosity can be determined from a knowledge of the percentage distilling up to 355°C and the viscosity of two of the creosotes.

An attempt was made to apply the same reasoning to materials boiling above and below other temperature limits, as shown in Figs. 4 and 5, but it was found that the above relationship was not applicable in any of these cases. This does not necessarily mean that no other distillation temperature could be found to satisfy the above equation but it remains that under the standard practice of creosote distillation analyses the relation can only be applied to the materials boiling above and below 355°C. An interesting point disclosed by the curves of Figs.

TABLE V. θ is the constant of the Arrhenius equation and in this case is equal to the $\log_{10}$ [viscosity of the solution (creosote)/viscosity of the solvent (material distilling below 355°C)]/concentration of solute (material boiling above 355°C).

Sample No.	θ 40°C	θ 60°C	θ 80°C	θ 100°C
F–1	1.38	1.10	0.85	0.72
F–2	1.41	1.09	0.88	0.71
F–3	1.32	1.04	0.83	0.67
F–4	1.42	1.13	0.89	0.73
F–5	1.44	1.14	0.93	0.72
F–6	1.47	1.14	0.85	0.71
F–7	1.46	1.15	0.82	0.62
F–8	1.37	1.01	0.87	0.42

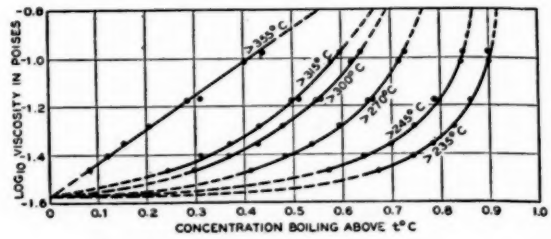

FIG. 4. Viscosity-concentration diagram for Fulweiler creosotes, viscosities at 40°C.

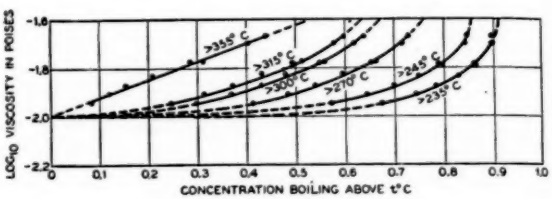

FIG. 5. Viscosity-concentration diagram for Fulweiler creosotes, viscosities at 100°C.

4 and 5 is the fact that the curvature increases as the temperature at which the theoretical cut has been made is decreased. Although it is realized that it is not permissible to extrapolate curves of this type to any great distance, the curves have been extended to zero concentration of material distilling below the designated temperatures. It can be noted from the diagrams that the curves tend to converge to a point which has been made to coincide with the value of F–9. This has been accomplished without in any way distorting the general curvature. Assuming that this method of extrapolation can be followed, it can be stated that any of the constituents boiling below 355°C when in solution in these creosotes must have a very similar effect on the viscosity of the whole solution. It is obvious from the distillation analyses in Table I that the ratio of the various constituents in these creosotes must vary to a high order of magnitude. It is not possible to apply the same reasoning to temperatures above 355°C, as the distillation analyses were not carried above this point, but it is believed that very interesting information could be obtained by such a study.

A continuation of this investigation to include other series of creosotes as well as creosotes used in commercial practice should prove valuable in determining the utility of the above relationship in classifying these materials.

VI. The Correlation of the Distillation Range with the Surface Tension of Creosote*

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(Received March 14, 1935)

The surface tension of each of a series of creosotes distilled from a common tar has been determined at various temperatures. The surface tensions of the several creosotes do not differ substantially at any given temperature. Differences in the rates of penetration of such creosotes into capillary materials are regarded as due to differences in the viscosities or the solid-liquid contact angles. The Langmuir theory of surface phenomena has been applied to explain the similarity of the surface tension values.

INTRODUCTION

IMPREGNATION of fibrous materials with liquids is essentially a process of penetration into empty or partially filled capillaries. The rate at which the absorption of the liquid can take place is affected by the surface tension of the liquid at its entering boundary[1] as well as the viscous resistance of the liquid in the penetrated portions of the capillaries. The effect of the surface tension may be expressed as a force tending to cause flow either into or out of the porous medium depending on whether or not the material is wet by the liquid. When the liquid does wet the material the capillary pressure acts in the same direction as the applied external pressure and is an aid to penetration. The force promoting wetting is measured as the product of the surface tension and the cosine of the angle of contact between the liquid and solid. Foreign substances, such as free water, in the material to be impregnated may determine whether the impregnant will be wetting or nonwetting depending on changes in the contact angles brought about by their presence in the system.

Wood dealt with in preservation processes may have three distinct types of moisture distribution: (1) All the moisture is held as sorbed water; (2) some portions of the wood contain free water; and (3) all portions of the wood are above fiber saturation. In the first type of moisture distribution a high surface tension of impregnant is desirable as most wood preservatives wet wood which is below fiber saturation. When all the wood is above fiber saturation the surface tension forces of oily liquids may act in a direction opposite to the external pressure. In this case a high surface tension is undesirable. When only the interior of the wood is above fiber saturation the capillary forces may act in one direction near the surface and in the opposite direction in the interior. In wood in this condition a high surface tension is desirable for impregnation of the exterior portions of the wood whereas a low surface tension is preferable in the interior.

The importance of surface tension in the impregnation of wood is evident from the above considerations.

THEORY

The surface tension of a liquid is due to the cohesive action of the molecules composing it. In the body of the liquid a molecule is attracted equally in all directions, whereas a molecule in the surface of the liquid is attracted only inwardly by the molecules of the liquid within its sphere of influence. This results in a condition, the effect of which is similar to an elastic membrane stretched over the surface of the liquid and always tending to press inwards.

Liquids that wet glass will rise in a vertical capillary tube to a height which is dependent on the capillary pressure of the liquid and the counter pull of gravity. It was shown by Jurin that when equilibrium is reached

$$\gamma = rh\rho g/2 \cos\theta, \qquad (1)$$

where γ is the surface tension of the liquid, r is the radius of the capillary tube, h is the height of rise, ρ the density of the liquid, g the gravity constant and θ is the angle of contact between the liquid and the solid.

* This paper is one of a series entitled "Chemical Studies of Wood Preservation" being published in this journal and in Industrial and Engineering Chemistry.

[1] Hawley, U. S. Dept. Agr. Tech. Bull. **248**, June (1931).

Experimental

The apparatus used was essentially the same as that described by Richards.[2] It consisted of a carefully calibrated uniform capillary tube sealed to a larger tube in the form of a U. The capillary tube was calibrated in the usual manner by measuring the length of a weighed mercury thread at various positions in the tube and after correcting for the protrusion of the menisci, the radius was found to be 0.0268 cm. The radius of the large tube as measured at its open end with a cathetometer was 0.184 cm. The apparatus was held vertically in an oil bath maintained at the desired temperature with an accuracy of ±0.1°C by means of a mercury column thermostatic control.

Richards[2] has shown that the weight of the meniscus in the capillary tube should be considered in an accurate determination of the surface tension. He further showed that the meniscus in the larger tube of his apparatus should also be considered unless the tube is sufficiently large for the formation of a comparatively flat meniscus. The corrections made by him were based on the assumption that the meniscus is an oblate spheroid. The validity of this assumption was proved by Winkler[3] who weighed the meniscus. For the apparatus used in this investigation it can be shown that the height of rise of the liquid will be decreased by an amount equal to one-third the radius of the capillary minus one-third the height of the meniscus in the large tube. Eq. (1) then becomes:

$$\gamma = (r\rho g/2\cos\theta)(h_0 + r/3 - h_m/3), \qquad (2)$$

where h_m is the height of the meniscus in the large tube.

A suitable quantity of the liquid is pipetted into the apparatus and the whole allowed to remain in the bath at the desired temperature for at least 30 min. The glass above the meniscus is wet with the liquid by applying a slight suction to the capillary end of the apparatus. Readings of h_m and h_0 are made with a cathetometer after the meniscus has been allowed to fall to its equilibrium position. Other workers have shown that the use of a rising meniscus will not give concurrent results because of changing contact angles.

The surface tensions of freshly distilled water, benzene and aniline were checked in the above manner in order to determine the accuracy of the measurements. The results of these determinations are given in Table I.

Table I. *Surface tensions of the calibrating liquids.*

Temp. °C	h_m cm	Surface Tension (dynes/cm) Experimental Uncorr.	Corr.*	Literature†		% Error Uncorr.	Corr.
			Water				
30	0.151	71.44	70.81	71.18	±0.05	+0.37	−0.52
50	0.137	68.13	67.57	67.91	±0.05	+0.32	−0.50
			Benzene				
30	0.134	27.79	27.31	27.56	±0.05	+0.83	−0.91
			Aniline				
30	0.150	42.47	41.83	41.7	±0.4	+1.85	+0.31

* Corrected for the weight of the meniscus.
† International Critical Tables.

With the exception of the aniline value, which, in the literature is accurate to only about 1 percent, the uncorrected values of the surface tension of the calibrating liquids check the literature fully as well as the corrected values. From the fact that the corrected values are slightly lower and the uncorrected values slightly higher than those in the literature, it appears that the meniscus correction may be too large. This may be accounted for either by an inherent error in the calibration measurements of the instrument or a constant error in the measurement of the calibrating liquids.

This investigation of the surface tension is a part of the study of the physical properties of the Fulweiler series of creosotes[4] of various boiling ranges which were distilled from a common tar. Measurements of the heights of rise of these creosotes were attempted in the above manner but the menisci were obscured because of the color of the creosotes. The surface tension values of the creosotes, as given in Table II, have therefore not been corrected for the weight of the meniscus. Values of the surface tension

[2] Richards and Coombs, J. Am. Chem. Soc. **37**, 1656 (1915).
[3] Winkler, Zeit. f. angew. Chemie, 719 (1903); Zeits. anal. Chemie **40**, 403 (1901).
[4] Frosch, V. *The Correlation of Distillation Range With the Viscosity of Creosote*, Frosch, VII. *The Correlation of Distillation Range With the Interfacial Tension of Creosote Against Water.* In this issue.

TABLE II. *Surface tensions of Fulweiler creosotes at various temperatures.* The values of surface tension in brackets were determined by the drop volume method.

Sample No.	Residue* above 355°C-%	Surface Tension (dynes/cm) 40°C	60°C	80°C	100°C
F-1	43.84	38.35 (38.60)	36.41	34.54	33.66
F-2	40.25	37.70 (38.22)	36.07	34.39	32.76
F-3	31.11	37.59 (37.86)	35.63	33.85	32.24
F-4	28.52	37.46 (37.68)	35.88	33.52	32.44
F-5	20.85	37.41 (37.99)	35.57	33.90	31.99
F-6	15.49	37.49 (37.93)	35.53	33.81	32.37
F-7	12.21	37.52 (38.30)	35.41	33.64	31.39
F-8	8.49	37.01 (37.45)	35.30	33.47	31.73

* Standard Distillation of Creosote, Standard 11e, American Wood-Preserver's Association Manual of Recommended Practice.

determined by the drop-volume method[4] have been included in the same table for purposes of comparison.

The contact angles glass-creosote were not determined in this investigation but assuming they were small the calculations of the values in Table II were made by taking θ equal to 0. The assumption seems to be justified for the values calculated check very closely with those determined by the drop volume method. The latter method is independent of the contact angle.

DISCUSSION

The data indicate a slight increase in the surface tensions of the creosotes with an increase in high boiling material but it is entirely too small and too variable to warrant our consideration. Each creosote shows a decrease in surface tension with increasing temperature, and it may be said that the Fulweiler creosotes have equal values of surface tension at any given temperature without involving any serious error.

Washburn[5] has shown that for small capillaries

$$P = F(\eta, t, \gamma \cos \theta),$$

where P is the depth of penetration, η the viscosity of the liquid, γ the surface tension, t the time of submergence in the liquid and θ is the angle of contact between liquid and solid. Assuming this relation to be true it is obvious that, since the Fulweiler creosotes have equal surface tensions at the same temperature, any difference in their rate of penetration into a porous material must depend entirely on the viscosity providing the solid-liquid contact angles are the same for all of these creosotes. Later work on the penetration of these creosotes into paper strips[6] which are below fiber saturation has shown that viscosity is the only factor producing changes in the rate of their penetration at a given temperature.

According to Langmuir[7] and others, the structure of the surface layer of molecules is regarded as the principal factor in determining the surface tension of a liquid. The molecules of a liquid arrange themselves in the surface layer in such a way that their active portions are drawn inwards leaving the less active portions to form the surface layer. The surface tension is thus not a property of the molecules comprising the liquid but depends only on the least active portions of the molecules and the manner in which the molecules are able to arrange themselves in the surface layer. The similarity of the surface tensions of the Fulweiler creosotes can be attributed to similar orientation effects. It would follow that the surface layers of the creosotes contain molecules with similar inactive portions.

Some surface tension data which we have taken on several other diverse creosotes suggest that surface tension is rarely if ever an important distinguishing characteristic of creosote.

[5] Washburn, Phys. Rev. **17**, 273 (1921).

[6] Frosch, *The Correlation of the Distillation Range With the Penetration of Creosote Into Paper Strips.* To be published in Physics.

[7] Langmuir, Chem. Met. Eng. **15**, 468 (1916).

VII. The Correlation of Distillation Range with the Interfacial Tension of Creosote Against Water*

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Measurements of interfacial tension against water of each of a series of creosotes distilled from a single tar are reported. It is found that the interfacial tension values of these creosotes varied as much as 30 percent although no definite trend was present which could be related to other physical properties. Two possible theories to explain the differences in the interfacial tensions are discussed.

INTRODUCTION

SUBSTANTIALLY every important process which deals with the impregnation of a cellulosic material is affected by the presence of water. Regardless of whether the water is present as sorbed or free water, it has a marked influence on the impregnation process as well as the subsequent use of the treated material. The effects of sorbed water may be classed broadly as dimensional and adhesional. The former is operative in changing the rate of absorption of the liquid penetrant due to the effect of changing pore size (swelling) on the capillary pressure and the viscous resistance of the liquid. The latter may cause a change in the rate of penetration due to variations in the adhesion tension between liquid penetrant and solid as the latter is modified by the presence of sorbed water. The influence of free water on penetration is probably more important than that of sorbed water in most wood impregnation problems as it may change the wetting relations between the solid and the liquid penetrant. That is to say, the forces of interfacial tension between water and the liquid penetrant determine the contact or wetting angle between the liquid and the solid. However, since this part of the investigation is not concerned with the presence of cellulosic substance, it will suffice to limit the discussion to the forces acting between water and creosote at their interface.

The most obvious property of a mobile interface is its tendency to shrink to a minimum. Thus liquid drops suspended in another liquid assume a spherical form in the absence of extraneous forces of gravity. The boundary seems to be the seat of a contractile force called interfacial tension.

The spreading characteristics of liquids may best be illustrated by a consideration of the energy change involved when a liquid (A) spreads over a liquid (B) upon which it floats. In the absence of solubility and external forces, the change in free energy or the work involved per unit area when A spreads over B is

$$W_S = \gamma_B - \gamma_{AB} - \gamma_A,$$

where γ_A and γ_B are the surface tensions of A and B, respectively, while γ_{AB} is the interfacial tension between the two liquids. The condition necessary for spontaneous spreading to occur depends upon a positive value of W_S, i.e., $\gamma_B > \gamma_{AB} + \gamma_A$. A negative value of W_S, will cause A to remain on B in the form of a lens.

Harkins[1] has pointed out that work of spreading is equal to the adhesional work of A and B minus the cohesional work of A, i.e., $W_a - W_c$; this quantity is the "initial spreading coefficient." It is evident that the adhesional forces acting between two liquids are directly dependent on their interfacial tension. Thus a high interfacial tension is conducive to a low value of adhesion between two liquids and spreading will not take place unless the cohesive forces of the spreading liquid are small. The importance of a study of interfacial tension is obvious in penetration problems concerned with the presence of free water.

APPARATUS

The drop-volume method of measuring the interfacial tension was selected, since in a method

* This paper is one of a series entitled "Chemical Studies of Wood Preservation" being published in this journal and in Industrial and Engineering Chemistry.

[1] Harkins and Feldman, J. Am. Chem. Soc. **44**, 2665 (1922).

of this type a very simple form of apparatus will give reliable data. The apparatus consists of a 5 cm³ measuring pipette connected by a length of capillary tubing to an accurately machined dropping tip. The vertical sides of the tip were highly polished to minimize wetting by the dropping liquid whereas the horizontal dropping surface was roughened to insure complete wetting by the liquid over the entire cross section. The upper end of the pipette is connected to a large air reservoir which in turn is sealed to two three-way stopcocks connected in series by a small glass tube. By means of this arrangement, the rate of drop formation can easily be controlled by the addition or removal of small amounts of air.

The apparatus, with the exception of the regulating stopcocks, was vertically suspended in an air bath maintained at 39.4°C with an accuracy of ±0.1° by means of a mercury column thermostatic control. The stirring was accomplished by means of a motor-driven propeller.

Experimental

After careful heating and mixing of the creosote to assure a uniform sample, the pipette is filled to above the graduations by submerging the tip in the sample and applying a slight suction at the open end of the stopcock system. The smooth portion of the tip is then carefully cleaned so that the drops do not become too large because of an increased area of suspension. In surface tension measurements, the tip is enclosed in a small vessel to minimize evaporative losses and to assure liquid-vapor contact during a determination. The measurements are made after the lapse of one and one-half hours. The drops are allowed to fall at a rate of less than one drop per minute. At least 20 drops are counted in this manner and the measurements of volume taken after each tenth drop. This is done to insure uniformity in size of drops. Variation is usually due to an unclean tip which produces unsymmetrical drops.

In the case of measurement of interfacial tension against water, a drop is allowed to form and the tip is then submerged beneath the surface of freshly distilled water in a small container. It is essential to do this to insure initial wetting of the dropping surface by creosote rather than water. Otherwise the drops of creosote are unsymmetrical and determinations vary greatly.

Measurements are made after the lapse of at least one and one-half hours during which time three or four drops are allowed to form thus assuring the saturation of the water phase with the constituents of the creosote. A volume reading is taken after each five drops and in this case, as above, the determination is repeated when checks are not considered satisfactory. The time of drop formation should exceed 2 minutes to secure uniformity in size of drops and saturate at least the surface of the drops with water.

The calculations of the tensions are made by the use of the following equation:

$$\gamma=[V(\rho_1-\rho_2)g/R]F, \qquad (3)$$

in which V is the volume of the drop, ρ_1 is the density of the liquid to be measured, ρ_2 is the density of the medium in which the drops are forming, g is the gravity constant, R is the radius of the dropping surface of the tip (0.244 cm in this case) and F is a function of V/R^3 which Harkins[2] has empirically determined by a comparison with the capillary rise method.

The measurements were checked by comparing the data in the literature with the experimentally determined values of the surface tension of water and the interfacial tension of benzene against water. The results are tabulated in Table I.

The experimentally measured values of the surface tension and interfacial tension against

Table I. *Tensions of calibrating liquids at 39.4°C.* Phase *A* represents the dropping liquid to be measured while phase *B* is the medium in which the drops are forming.

	Phase *B*					
	Air Vapor			Water		
Phase *A*	Obs.	Lit.	Error	Obs.	Lit.	Error
Benzene				34.36	33.86*	+1.48%
Water	69.94	69.66*	+0.40%			

* These values were taken from the *Sixth Colloid Symposium*, (1928), p. 25; and are data by Harkins and Cheng.

[2] Harkins and Brown, J. Am. Chem. Soc. **41**, 499 (1919).

TABLE II. *Tensions and drop volumes of the Fulweiler creosotes at 39.4°C.*

Sample No.	Residue* above 355°%	Abs. Dens. 39.4°C	Vapor		Water	
			V (cm³)	γ	V (cm³)	γ
F–1	43.84	1.0898	0.0335	38.66	0.2006	18.44
F–2	40.25	1.0850	0.0333	38.22	0.1816	15.98
F–3	31.11	1.0723	0.0334	37.92	0.2382	17.74
F–4	28.52	1.0701	0.0333	37.74	0.2190	15.96
F–5	20.85	1.0645	0.0338	38.04	0.2831	18.79
F–6	15.49	1.0556	0.0340	37.99	0.2885	16.76
F–7	12.21	1.0514	0.0345	38.36	0.3489	18.70
F–8	8.49	1.0425	0.0340	37.50	0.4835	21.66

* Standard Distillation of Creosote, Standard 11e, American Wood-Preserver's Association Manual of Recommended Practice.

water of the Fulweiler creosotes used in previous studies on viscosity and surface tension[3] are given in Table II. The changes in the density of water and creosote phases caused by their slight mutual solubility were regarded as negligible.

DISCUSSION

Although the interfacial tension values of the Fulweiler creosotes against water do not show any definite trend that can be related to the distillation range, there is a spread of approximately 30 percent among the values for the eight creosotes. This variation in interfacial tension against water would cause the creosotes to have unequal contact angles in the capillary pores of wood above fiber saturation and their rate of penetration would be affected accordingly.

It should be noted that the interfacial tension values as determined are not the tension values of the original liquids but are the values of wet creosote against oily water. Such a mutual solution of the phases undoubtedly alters the true interfacial tension, although the very nature of this or any similar method makes it impossible to eliminate this effect. In the impregnation of capillaries containing free water, the tensions are also between oily water and wet oil although equilibrium conditions are not fully assured in either case.

It was hoped that some explicit difference in the Fulweiler creosotes might explain the variations in the interfacial tension values. All other disparities among the creosotes, revealed by the present types of analyses, showed definite trends depending on the temperature of distillation of the creosotes from the tar. It is possible that the erratic deviations of the interfacial tension values are due to the presence of small and varying amounts of an extremely active constituent. Such a material would probably be present in too small a concentration to be detected by ordinary analyses and may indeed be extremely difficult to detect by more exact analyses due to the innumerable components contained in creosote. The preferential adsorption of such an extremely active material in the interface could bring about gross changes in the interfacial tensions.

The effect of adsorption in the interface is demonstrated by the emulsifying action of certain well-known materials such as stearates, oleates, etc. The adsorption of small amounts of these materials in the interface causes a decided decrease in the interfacial tension between water and oil and hence allows the formation of small drops of one medium in the other. An example is found in the reported use of lecithin in the impregnation of poles with creosote.[4] In this case the adsorption of the lecithin in the interface between creosote and water, when wood above fiber saturation is impregnated, is said to decrease the interfacial tension and hence to increase the wetting or penetrating power of the creosote. Materials added to impregnants to increase their penetrating power have been referred to as "introfiers."[5]

According to Harkins[6] and Langmuir[7] the molecules of a liquid arrange themselves in the interface in such a way that the active portions extend into the water phase while the inactive portions project into the oil. It is readily understandable that when a molecule contains more than one active group, a tilting of the whole molecule may be necessary to satisfy the above conditions. The latter may result in changes in the interfacial tensions. The interfacial tension of an oil mixture is thus not a property of the oil as a whole but depends on the presence of active molecules and the type, number and distribution

[3] Frosch, *The Correlation of Distillation Range With the Viscosity of Creosote; The Correlation Distillation Range With the Surface Tension of Creosote.* In this issue.

[4] Vaughan, Proc. Am. Wood-Preserver's Ass'n, 188 (1934).

[5] Darrin, Ind. Eng. Chem. **20**, 801 (1928).

[6] Harkins, Brown and Davies, J. Am. Chem. Soc. **39**, 354 (1917).

[7] Langmuir, Chem. Met. Eng. **15**, 468 (1916).

of active groups in them since these determine how these molecules arrange themselves with respect to the water phase. Assuming that the hydroxyl group is the most active group in creosote, it might be expected that the interfacial tension would increase with volatility since analyses have shown that the phenolic constituents are more abundant in the lower distillation ranges. Such a regular increase in the interfacial tensions is not present but the variations may be due to the distribution of specific phenols of high activity among these creosotes. The study of the interfacial tensions of other creosotes as well as investigations of the effect of additions of other compounds may well lead to an explanation of the irregularities noted.

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Errata: The Theory of Non-Newtonian Liquids

MARKUS REINER, *Department of Public Works, Jerusalem*

(Physics **5**, 321, 1934)

THE following corrections should be made:

In all cases θ should be ϑ.

Page 323: Seventh line after Eq. (6) should end with "deformation."

330: Left-hand Eqs. (33) and (34), d should be v_d.

335: Section 14, line 21, should have "(c)" inserted before "this."

339: Col. 1, paragraph (b) should begin: "The interference with the deformation of the liquid produces by reaction in the particle tensional stresses."

Col. 2, fourth sentence of paragraph (c) should be: "Rotation of the particle tends to restore an agglomeration."

340: Table II, under 1d, "Adsorption" should be "Shortening."

Col. 2, line 14, (2b, 8) should be (2b, δ).

341: Section 18, line 15, "vibration" should be "variation"; line 24, "(a)" should be "(1a)"; lines 35 and 36, "(b), (c), (d)" should be "(β), (γ), (δ)."

Errata: Viscometric Studies of Rubber Solutions

MARKUS REINER, *Department of Public Works, Jerusalem*

(Physics **5**, 342, 1934)

THE following corrections should be made:

Page 345: Eqs. (13) and (14), p should be β.

Col. 2, second from last line, delete "between the."

347: Eq. (9), $2\xi^2\eta^2$ should be $2\xi^2-\eta^2$.

LETTERS TO THE EDITOR

This section will accept brief reports of new work of general interest to industrial physicists. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the fifteenth of the month preceding that of the issue in which the letter is to appear.

The Propagation of Rayleigh Waves in Heterogeneous Media—an Addition

In a recent paper,[1] dispersion curves were given for Rayleigh waves in three heterogeneous elastic media where $\lambda=\mu$ and $(\rho/\rho_0)=(\mu/\mu_0)=(\lambda/\lambda_0)=\cosh^2\beta z$, $e^{2\beta z}$, $(1+\beta z)^2$, respectively. These curves were plotted in the conventional manner against the wavelength. However, the wavelength of a periodic seismic wave is not a directly observable quantity, since, while we may determine approximately the period and the velocity, the latter is the group velocity and not the phase velocity. We have therefore replotted our curves against the period $T=L/v$, L being the wavelength and v the phase velocity, as shown in Fig. 1.

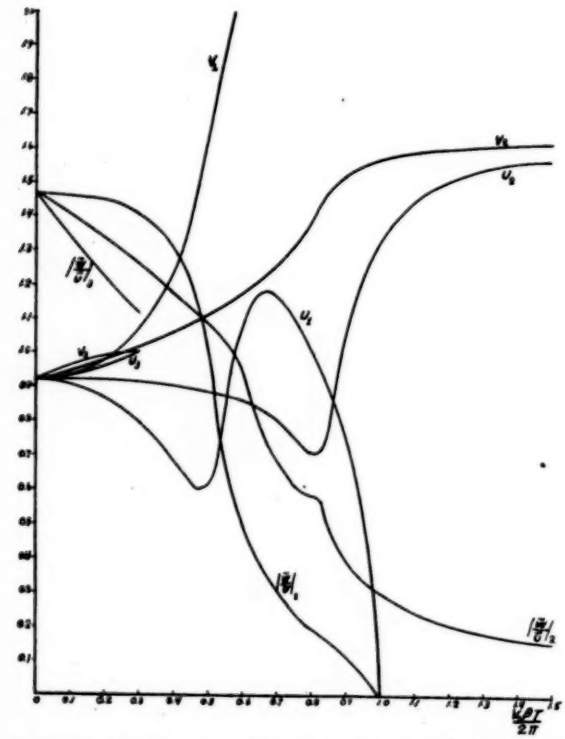

FIG. 1. Rayleigh wave velocities and surface-amplitude ratios in media 1, 2 and 3, in which $\lambda=\mu$ and $(\rho/\rho_0)=(\mu/\mu_0)=(\lambda/\lambda_0)=\cosh^2\beta z$, $e^{2\beta z}$, $(1+\beta z)^2$, respectively. v and u denote the Rayleigh wave velocity and group velocity in units of v_0, the shear wave velocity at the surface. T is the period in seconds; $|\bar{w}/\bar{u}|$ denotes the absolute value of the ratio of the vertical to the horizontal amplitudes at the surface. The maximum period in medium 3 is $0.2989(2\pi/\beta v_0)$.

The distinguishing features of these curves as compared with corresponding curves for media made up of homogeneous layers are: (1) The monotone decrease of $|\bar{w}/\bar{u}|$ with period; (2) the existence, in some media, of an upper limit to the period; and (3) the existence in medium 1 of two wavelengths at which the derivative of the group velocity with respect to the period, and therefore also with respect to the $(1/L)$, vanishes.

These new features strongly suggest the following observed statistical characteristics of the M waves in normal earthquakes:[2] (1) The most frequent values of $|\bar{w}/\bar{u}|$ range from 0.90 to 1.40 as against the value of 1.47 for a homogeneous medium.[3] (2) The existence of an upper limit to the period at large epicentral distances,[4] and (3) The preponderance of waves of period 18 sec. and 12 sec. at Göttingen.[5]

It appears, therefore, that a medium made up of layers of constant velocity, but with density and elastic constants increasing with depth, may be characterized by Rayleigh waves which resemble the observed M waves of normal earthquakes more closely than do the waves propagated by a medium made up of homogeneous layers.

CHAIM L. PEKERIS

Massachusetts Institute of Technology,
April 30, 1935.

[1] C. L. Pekeris, Physics **6**, 133 (1935).
[2] B. Gutenberg, *Handbuch der Geophysik*, 1932, Vol. **IV**, p. 242.
[3] C. Mainka, Phys. Zeits. **16**, 117 (1915).
[4] K. Wegener, Gött. Nach. 1913, No. 3; J. B. Macelwane, Bull. Seism. Soc. America **18**, 13 (1923); B. Gutenberg, reference 2, p. 243.
[5] F. Roesener, Gerl. Beit. z. Geophysik **12**, 207 (1913).